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Research paper

Novel strategy for palygorskite/poly(acrylic acid) nanocomposite hydrogels from bi-functionalized palygorskite nanorods as easily separable adsorbent for cationic basic dye

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ABSTRACT

A novel strategy was developed for the preparation of a palygorskite/poly(acrylic acid) nanocomposite (Pal/PAA) hydrogel with a 3-D network structure, by the surface-initiated redox radical solution polymerization of acrylic acid (AA) with the bi-functionalized palygorskite (BF-Pal) nanorods, in which the amino groups acted as the initiating groups, and the C═C groups acted as the crosslinking groups. The effect of the synthesis conditions on the component in the Pal/PAA nanocomposite hydrogels were investigated with TGA analysis. The designed Pal/PAA hydrogel exhibited a remarkably high adsorption capacity for methylene blue (MB) of 833.9 mg/g.

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1. Introduction

Hydrogels with three-dimensional (3-D) network structure are well documented to be used for the removal of heavy metals and/or toxic organic compounds from aqueous solutions, due to their large number of functional groups (Dragan, 2014). They could swell considerably in aqueous medium without dissolution. This feature is helpful for adsorbing and trapping of certain pollutants. Furthermore, their unique swelling property and porous network structure allow these contaminants more easily access to the functional groups on the hydrogels.

Recently, it has been reported that the composite hydrogels showed the higher mechanical strength, thus their cycling property had been improved obviously (Jiang and Liu, 2014; Jing et al., 2013; Liu et al., 2014; Luo et al., 2010; Xiang et al., 2006), especially for those with the inorganic materials as covalently crosslinking sites (Chen et al., 2011a, 2011b; Jiang and Liu, 2014; Liu et al., 2014; Luo et al., 2010; Messing et al., 2011; Xiang et al., 2006; Zhao and Cao, 2012). Normally, there are two main approaches for the synthesis of composite hydrogels with a 3-D inorganic–organic network skeleton. One is the in-situ formation approach, in which the copolymer containing the functional unit such as γ-methacryloxypropyltrimethoxysilane was hydrolyzed to form the crosslinking structure (Zhao and Cao, 2012). The other one is the in-situ emulsion or suspension radical polymerization in the presence of the carbon nanotubes (Luo et al., 2010) or functionalized inorganic materials such as palygorskite (Liu et al., 2014; Xiang et al., 2006), fly ash (Jiang and Liu, 2014), Fe_3O_4 nanoparticles (Chen et al., 2011b), or $CoFe_2O_4$ nanoparticles (Messing et al., 2011). In the polymerization, more than one chain radicals could react with the polymerizable groups immobilized on the inorganic materials, thus the 3-D crosslinking network structure is achieved, with the organic phase (polymer) as the main component in the resultant composite hydrogels.

In previous work, high clay mineral-content palygorskite/poly(acrylic acid) (Pal/PAA) nanocomposite hydrogel with a 3-D network structure and clay mineral content of around 90% were synthesized by a novel surface-initiated redox radical solution polymerization of acrylic acid (AA) with the 3-aminopropyltriethoxysilane (APTES) modified palygorskite nanorods (Pal-NH_2) as initiator and the 3-methacryloxypropyltrimethoxysilane (MPTMS) modified palygorskite nanorods (Pal-C═C) as crosslinker (Zhu et al., 2014). The adsorption capacity of the cationic dye (methylene blue (MB)) of 308.0 mg/g was achieved when being used as the adsorbent for water treatment.

Here, both two functional groups (amino and vinyl groups) acting as initiators and crosslinkers were immobilized onto the same palygorskite nanorods in order to simplify the production process of the Pal/PAA

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nanocomposite hydrogel adsorbent. The bi-functionalized palygorskite (BF-Pal) nanorods, surface-functionalized with both APTES and MPTMS, were used to play both the initiating and crosslinking roles in the facile surface-initiated redox radical solution polymerization of AA (Fig. 1). The synthesis conditions, such as the APTES/MPTMS feeding ratio for the BF-Pal nanorods, the BF-Pal/AA feeding ratio, and the amount of ceric ammonium nitrate (CAN), on the component of the 3-D structured Pal/PAA nanocomposite hydrogels were investigated. The adsorption property toward MB and separation were also studied preliminarily.

2. Experimental section

2.1. Materials and reagents

Purified palygorskite powder was obtained from R&D Center of Xuyi Attapulgite Applied Technology, Lanzhou Institute of Chemical Physics, CAS.

Acrylic acid (AA) was analytical reagent obtained from Tianjin Kaixin Chemical Industry Co. Ltd., China. 3-Aminopropyltriethoxysilane (APTES) and 3-methacryloxypropyltrimethoxysilane (MPTMS) were provided by Jiangsu Chenguang Silane Co., Ltd., China. Ceric ammonium nitrate (CAN, $(NH_4)_2Ce(NO_3)_6$) and other reagent used were all analytical-reagent grade, obtained from Tianjin Chemicals Co. Ltd. (Tianjin, China). Distilled water was used throughout.

2.2. Surface modification of palygorskite nanorods

After being baked at 180 °C for 12 h to remove any organic compounds, the palygorskite powder was grinded in distilled water into Pal nanorods and then activated by acidification in 4.0 mol/L HCl (Yang et al., 2010).

2.0 g activated Pal nanorods and certain amounts of the silanes (Table 1) were dispersed into 40 mL absolute alcohol by ultrasonication for 2 h. Then the mixture was refluxed for 24 h with magnetic stirring. The product was separated by centrifugation and washing with ethanol for three times to removal the excess silanes. The bi-functionalized palygorskite (BF-Pal) nanorods (BF-Pal_1, BF-Pal_2 and BF-Pal_3) were dried in vacuum at 40 °C for 24 h.

Table 1
Surface-modification of Pal.

	Pal (g)	MPTMS (mL)	APTES (mL)	EtOH (mL)
BF-Pal_1	2.0	0.25	0.25	40
BF-Pal_2	2.0	0.15	0.35	40
BF-Pal_3	2.0	0.35	0.15	40

2.3. Surface-initiated redox radical solution polymerization

0.40 g of the BF-Pal nanorods (BF-Pal_1, BF-Pal_2 or BF-Pal_3) was dispersed into 2.0 mL water. After certain amount of AA and CAN were added (Table 2), the mixture was stirred in N_2 atmosphere at 60 °C for 20 h. The obtained Pal/PAA nanocomposite hydrogel particles were extracted with water for 24 h using Soxhlet apparatus to remove any ungrafted PAA (Mansoori et al., 2010), and dried in vacuum at 40 °C.

2.4. Adsorption performance

5.0 mL aqueous dispersion containing 9.72 mg of Pal_1/PAA-8 nanocomposite hydrogel particles was charged into 95.0 mL MB aqueous solution at different pH values (2.0, 3.0, 4.0, 5.0, 6.0 or 7.0). After stirring for 180 min, part of the supernatant solutions was taken out for detection to measure the uptake with UV–vis spectrophotometer (Lambda 35, Perkin Elmer Corporation, USA) at 665 nm, equipped with a 10 mm path length quartz cell. Each value represents the mean (SD < 1%, n = 3).

2.5. Analysis and characterization

Bruker IFS 66 v/s infrared spectrometer was used for the FT-IR analysis in the range of 400–4000 cm^{-1} with resolution of 4 cm^{-1}. The KBr pellet technique was adopted (1 mg per 150 mg sample). A total of 60 scans were accumulated.

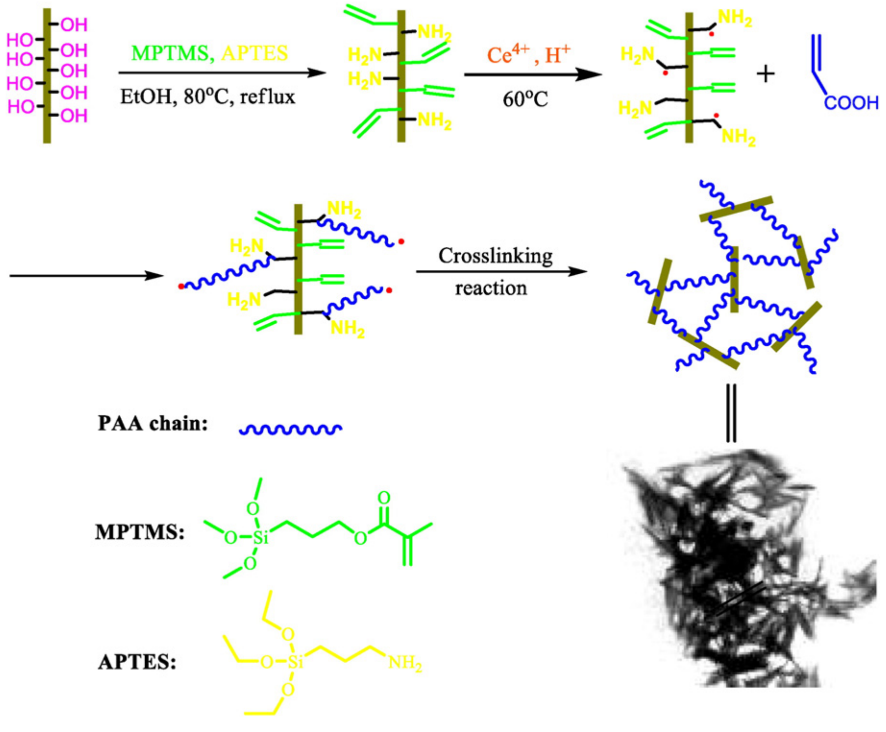

Fig. 1. Schematic illustration of the developed strategy for the novel Pal/PAA nanocomposite hydrogels.

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